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G01N

(54) Gas sensing device

(57) A conductimetric gas sensing device comprises: an ion exchange layer 4 of porous material for saturation with water; means for measuring the conductance of the ion exchange layer; and a gas permeable membrane 5 impermeable to liquids arranged to separate the ion exchange layer from a test fluid 6 such that gas present in the test fluid diffuses through the membrane and dissolves into the ion exchange layer modifying its conductivity. The ion exchange layer 4 may be equimolar in anionic and cationic groups to act as a pH buffer, and may be formed from a polymer or a zwitterion species.

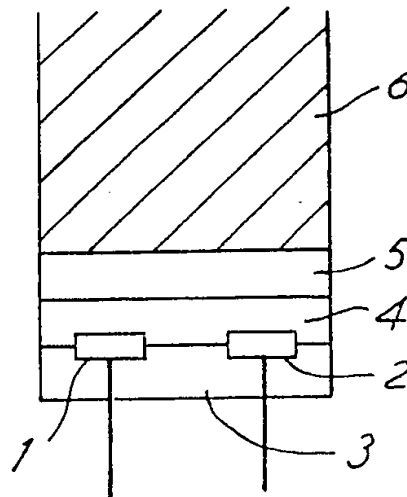


FIG.1

The drawing(s) originally filed was (were) informal and the print here reproduced is taken from a later filed formal copy

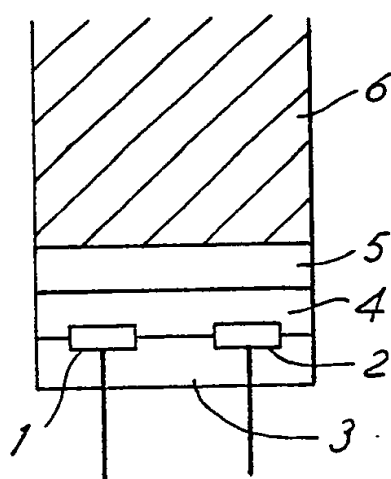


FIG. 1

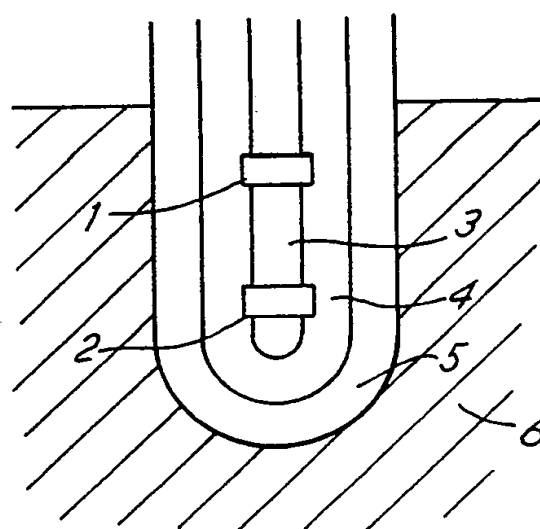


FIG. 2

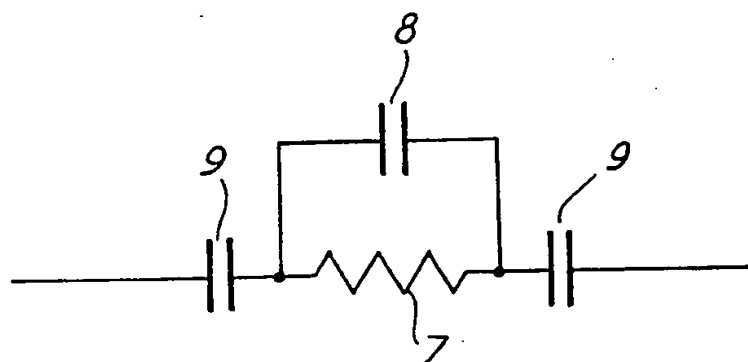


FIG. 3

: 1 :

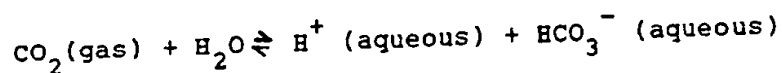
"GAS SENSING DEVICE"

This invention relates to a gas sensing device and, in particular, to a conductimetric gas sensing device, that is a gas sensing device which determines the partial pressure of a gas in a fluid sample by measuring the conductance of an aqueous solution in which the concentration of the gas is in equilibrium with the fluid sample.

One form of conductimetric gas sensor is described by J.S. Symanski et al in the paper "Conductimetric Sensor for Atmospheric Carbon Dioxide" in Analytical Chemistry Vol. 55, No. 7, June 1983, pp 1152-1156. This sensor comprises a hydrophobic gas porous membrane which separates the gas sample from a thin layer of an aqueous phase. The gas diffuses through the membrane, to form an equilibrium concentration in the aqueous layer, thereby increasing the conductance of the aqueous layer. It is known both from theory and measurement that the specific conductivity k of the aqueous layer in such a device is proportional to the square root of the partial pressure of the gas in the fluid sample, for example $p\text{CO}_2$ for carbon dioxide. The relationship is in the form:

$$k = 10^{-3} (\lambda_{\text{H}^+}^{\circ} + \lambda_{\text{HCO}_3^-}^{\circ}) (K_1 \cdot p\text{CO}_2)^{1/2}$$

where λ_i° is the equivalent ionic conductance of the species i at infinite dilution and K_1 is the equilibrium partition constant in the reaction:



The non-linearity of the relationship between the specific conductivity k and the partial pressure of gas in the test fluid sample can be a disadvantage of such a conductimetric gas sensing device. This is particularly so when small concentration changes about mean levels are of interest as, for example in clinical CO_2 measurement, the square root dependence represents a severe limitation on the usable dynamic concentration range of the sensor.

It is therefore an object of the present invention to provide a conductimetric gas sensor in which the measured conductivity is linearly related to the partial pressure of the gas in the fluid sample and which consequently has a high and uniform sensitivity to small differences in the partial pressure, and hence concentration, of the gas in the fluid sample over a wide range of partial pressures.

According to the present invention there is provided a conductimetric gas sensing device comprising:

an ion exchange layer of porous material for saturation with water;

means for measuring the conductance of the ion exchange layer; and

a gas permeable membrane impermeable to liquids arranged to separate the ion exchange layer from a test fluid such that gas present in the test fluid diffuses through the membrane and dissolves into the ion exchange layer modifying its conductivity.

Preferably, the ion exchange layer is equimolar in anionic (A^-) and cationic (BH^+) groups, to act as a pH buffer with

respect to changes induced by dissolving an acidic or basic gas therein.

In one embodiment of the invention the ion exchange layer is formed from a polymer.

5 In an alternative embodiment of the invention the ion exchange layer is formed from a zwitterion species comprising at least one of each of an anionic and a cationic group.

Preferably, one surface of the ion exchange layer is arranged to be in contact with a pair of electrodes attached to an inert,
10 electrically insulating substrate, to provide the means to measure the conductance of the said ion exchange layer.

In a preferred embodiment of the invention the ion exchange layer is disposed upon a layer of the substrate the said substrate being provided with the electrodes.

15 In an alternative embodiment of the invention the ion exchange layer is formed in a coating around a rod of the substrate provided with the electrodes.

The invention will now be described by way of example only and with reference to the accompanying drawings, of which:-

20 Figure 1 shows an arrangement in accordance with one embodiment of the invention,

Figure 2 shows an arrangement in accordance with an alternative embodiment of the invention,

Figure 3 shows an equivalent circuit for the arrangement of
25 Figures 1 or 2.

In the arrangement shown in Figure 1, electrodes 1 and 2 are formed on or attached to an electrically insulating substrate 3.

The electrodes 1 and 2 are in contact with one side of an ion exchange layer 4, which is saturated with water before use. A retaining layer 5 is permeable to gases or vapours, but not to liquids. It is formed on, or attached to, the layer 4 and prevents the layer 4 from having any direct contact with a test fluid 6. The electrodes 1 and 2 are connected to an a.c. supply providing a low voltage, typically of the order of 100mV, at a frequency of the order of 10 kHz where the electrical resistance of the absorbed water dominates over the effects of series and parallel capacitances.

The purpose of the ion exchange layer 4 is to buffer the ionic concentration changes induced by the dissolving gas and hence linearise the relationship between gas partial pressure and conductivity in the aqueous phase. This layer, which preferably is equimolar in cationic, BH^+ , (e.g. amino) and anionic, A^- , (e.g. carboxyl) ion exchange groups and by itself makes minimal contribution to the conductivity of the aqueous phase, may be formed in the following ways.

First, the ion exchange material may be polymeric (e.g. polyacrylic or polystyrene based) and formed in a manner analagous to conventional ion exchange resins but either from an equimolar mixture of functional monomers carrying on the one hand anionic and on the other cationic functional groups or from a functional monomer carrying anionic and cationic functional groups in equimolar proportions. Second, the ion exchange material may be formed by anchorage, either of an equimolar mixture of functional groups carrying on the one hand anionic and on the other cationic

functional groups plus a chemical linkage group or of a functional unit carrying both anionic and cationic exchange groups in equimolar proportions plus a chemical linkage group, to a previously formed porous support material. Examples of
5 established anchorage methods are silane linkage to a porous glass support and amide linkage between an amino group and an activated carboxyl group, the one or the other being part of an immobile support matrix. The resins formed by the above methods will be equimolar or thereabouts in immobile anionic and cationic exchange
10 groups.

Alternatively, monomeric or oligomeric rather than polymeric chemical units carrying anionic and/or cationic functional groups may be entrapped within a polymer gel matrix (e.g. poly-hydroxy-ethyl-methacrylate), by performing the conventional
15 polymerisation and/or crosslinking process for formation of the gel in the presence of amounts of the anion and cation carrying units. The polymer matrix may be formed with an appropriate pore size so as to restrict the mobility and hence associated conductivity of the anion and cation carrying units whilst
20 allowing relatively free migration of the smaller ion derived from the dissolving gas, which is to be determined. In this case the ion exchange groups may not be completely immobile but their mobility may be sufficiently restricted compared with that of the mobile gas derived ion that the observed conductivity will be
25 primarily due to the latter.

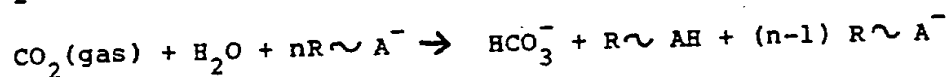
In each of the above cases the anionic and cationic groups within the ion-exchange layer 4 can act as a pH buffer with

respect to the changes induced by dissolving an acidic or basic gas therein.

If the test fluid 6 contains an acidic gas, for example carbon dioxide, the water absorbed in the layer 4 becomes acidic. Some of the anionic groups (A^-) then acquire an H^+ ion, forming immobile AH groups and an equal number of mobile negatives ions (eg HCO_3^-) in the water layer resulting in a equilibrium with

$$[HCO_3^-] = (K_2/[H^+])pCO_2$$

10 where K_2 is the equilibrium partition constant in the reaction



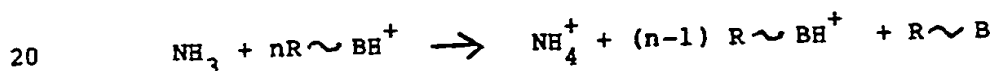
The specific conductivity k of the water in the ion exchange layer is then given by the equation

$$k = 10^{-3} \lambda_{HCO_3^-}^o (K_2/[H^+])pCO_2 \quad - - - (1)$$

15 A similar situation applies for a basic gas, for example ammonia, but involving the cationic exchange group BH^+ the equilibrium being given by

$$[NH_4^+] = (K_3/[H^+])pNH_3$$

where K_3 is the equilibrium partition constant in the reaction



and the specific electrical conductivity being given by

$$k = 10^{-3} \lambda_{NH_4^+}^o + (K_3/[H^+])pNH_3 \quad - - - (2)$$

Equations (1) and (2) show the linear relationship between the specific electrical conductivity and the partial pressure of the gas being measured, subject to the constraint that the immobile buffer ion is in sufficient excess to maintain $[H^+]$ effectively
 5 constant.

As an alternative to polymeric, monomeric and oligmeric materials, the ion exchange layer may instead be formed from a zwitterion species. A zwitterion species is a chemical which possesses at least one of each of a negative and a positive ion,
 10 so that over all it is electrically neutral. In this particular instance the zwitterion species carry both cationic (BH^+) and an ionic (A^-) groups in equimolar proportions (A^-BH^+) so as to carry, in the main, a net charge of zero over their effective operating range (e.g. glycine or other aminoacids around pH7), and
 15 may be employed either in immobile form as described previously or as freely diffusing species. In this freely diffusing case, if the test fluid 6 contains an acidic gas, for example carbon dioxide, such that the water absorbed in the layer 4 becomes acidic, then some of the anionic groups of the zwitterion acquire
 20 an H^+ ion, forming mobile positive $AH-BH^+$ groups and an equal number of mobile negative ions (e.g. HCO_3^-) in the water layer. The change in specific conductivity, k , of the aqueous phase in the ion exchange layer on exposure to a change in carbon dioxide partial pressure, pCO_2 , is then due to changes in the
 25 concentration of both bicarbonate and $AH-BH^+$ and is given by

$$k = 10^{-3} (\lambda_{HCO_3^-}^0 + \lambda_{AH-BH^+}^0) (K_2 / [H^+]) pCO_2$$

subject to the constraint that the zwitterion is in sufficient excess to maintain H^+ effectively constant. A similar situation applies for a basic gas.

An alternative embodiment of the invention is shown in the arrangement in Figure 2, in which the reference numerals correspond with those in Figure 1. In this arrangement the substrate 3 comprises a rod, carrying the electrodes 1 and 2, coated with the ion exchange layer 4 and the retaining gas permeable layer 5. This arrangement provides a probe suitable for immersion in a stationary or flowing liquid. Alternatively, the probe arrangement might comprise a flat substrate with successive layers on one or on both sides of it.

The equivalent circuit for the arrangement shown in Figure 1 or 2 is shown in Figure 3, where a resistor 7 represents the electrical resistance of the water in the ion exchange layer 4, a capacitor 8 represents the parallel capacitance of the ion exchange layer 4 and capacitors 9 represent the series capacitance between each of the electrodes 1 and 2 and the ion exchange layer 4. The resistance of resistor 7 can be measured accurately if the frequency f is sufficiently high for the effective series capacitance to have a negligible effect, but not so high that the parallel capacitance affects the measurement. A typical frequency for usual electrode geometries is of the order of 10kHz and the voltage of the a.c. supply is typically below 1V to avoid causing dissociation within the water held in the ion exchange layer.

The invention thus provides a conductimetric gas sensing

device with a linear response and the associated advantage of a wide dynamic range, making the sensor particularly suitable for measuring small changes in the concentration of a gas in a fluid as in, for example, measuring CO₂ concentrations in the blood.

- 5 The linear response of the device additionally makes for simple instrument calibration.

CLAIMS

1. A conductimetric gas sensing device comprising:
an ion exchange layer of porous material for saturation with
water;
means for measuring the conductance of the ion exchange
5 layer; and
a gas permeable membrane impermeable to liquids arranged to
separate the ion exchange layer from a test fluid such that gas
present in the test fluid diffuses through the membrane and
dissolves into the ion exchange layer modifying its conductivity.
- 10 2. A conductimetric gas sensing device according to Claim 1,
wherein the ion exchange layer is equimolar in anionic and
cationic groups, to act as a pH buffer with respect to changes
induced by dissolving an acidic or basic gas therein.
3. A conductimetric gas sensing device according to Claim 2,
15 wherein the ion exchange layer is formed from a polymer.
4. A conductimetric gas sensing device according to Claim 2,
wherein the ion exchange layer is formed from a zwitterion species
comprising at least one of each of an anionic and a cationic group.
5. A conductimetric gas sensing device according to anyone of
20 Claims 1 to 4, wherein the ion exchange layer is arranged to be in
contact with a pair of electrodes attached to an inert,
electrically insulating substrate, to provide the means to measure
the conductance of the said ion exchange layer.

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